

Some Complications Accompanying Electroreductions of Oximes

Petr Zuman¹ and Mara Aleksic²

¹Clarkson University
PO Box 5810, 8 Clarkson Ave
Potsdam, NY 13699
USA

²Department of Chemistry
PO Box 5810, 8 Clarkson Ave
Potsdam, NY 13699
USA

Some Complications Accompanying Electroreductions
of Oximes

Petr Zuman Department of Chemistry, Clarkson University, Potsdam, NY 13699-5810, USA

Mara Aleksic Department of Physical Chemistry, Faculty of Pharmacy, Vojvode Stepe 450, 11000, Belgrade, Yugoslavia

The traditional view of the reduction of oximes in aqueous buffered solutions is that it occurs at pH smaller than about 8 involving the protonated form of the oxime and a transfer of four electrons. The limiting current of the reduction of this protonated form decreases with increasing pH at pH greater than about 7. This decrease has the shape of a dissociation curve. In some instances, the reduction of the unprotonated form is observed at higher pH-values at considerably more negative potentials. For three compounds it has been reported in the literature that the four-electron wave is split into two two-electron waves, but no interpretation was offered for this phenomenon. Recently, it has been observed that the reduction of the O-methyl group of the antibiotic cefetamet results in a separation of two two-electron waves and this separation has been found to be a function of pH. The separation of the two waves in this case was demonstrated to be due to a difference in the plots of half-wave potentials as a function of pH for the parent oxime and the imine, formed as an intermediate. This difference is caused both by a difference in the pK_a values of the oxime and the imine and by differences in rates of protonation of the group C=NOH and the group C=NH. For this compound as well as a series of simple oximes, such as benzaldehyde oxime and acetophenone oxime, it was furthermore proved that at pH lower than about 4, where limiting currents of all these compounds are independent of pH, the limiting current in aqueous buffers decreases with increasing concentration of alcohols in the reaction medium. The measured currents show a tendency to limit to a value corresponding to a two-electron reduction. The decrease of the current is steeper and occurs at lower concentration of the alcohol in the sequence MeOH > EtOH > 2-PrOH > tBuOH. The reactivity of the alcohol thus increases with increasing nucleophilicity of the alcohol. The decrease is attributed to an addition of ROH to the C=NH grouping of the imine. Limits of equilibrium constants for these additions were estimated. Microcoulometric data obtained with DME indicate that even water is weakly added to the imine within the available time-window. The role of addition of other nucleophiles on the reduction of oximes is being investigated.